

Ab-initio study of the thermopower of biphenyl-based single-molecule junctions

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Employing ab-initio electronic structure calculations combined with the non-equilibrium Green's function technique we study the dependence of the thermopower Q on the conformation in biphenyl-based single-molecule junctions. For the series of experimentally available biphenyl molecules, alkyl side chains allow us to gradually adjust the torsion angle φ between the two phenyl rings from 0° to 90° and to control in this way the degree of π -electron conjugation. Studying different anchoring groups and binding positions, our theory predicts that the absolute values of the thermopower decrease slightly towards larger torsion angles, following an $a + b \cos^2 \varphi$ dependence. The anchoring group determines the sign of Q and a, b , simultaneously. Sulfur and amine groups give rise to $Q, a, b > 0$, while for cyano $Q, a, b < 0$. The different binding positions can lead to substantial variations of the thermopower mostly due to changes in the alignment of the frontier molecular orbital levels and the Fermi energy. We explain our ab-initio results in terms of a π -orbital tight-binding model and a minimal two-level model, which describes the pair of hybridizing frontier orbital states on the two phenyl rings. The variations of the thermopower with φ seem to be within experimental resolution.

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I. INTRODUCTION

Tailored nanostructures hold promise for improved efficiencies of thermoelectric materials.^{1–3} For this reason there is a growing interest to gain a better understanding of the role of interfaces on thermoelectric properties at the atomic scale. Controlled metal-organic interfaces can be studied using single-molecule junctions, and recently the thermopower of these systems was determined in first experiments.⁴ While the thermopower (or Seebeck coefficient) of metallic atomic contacts was measured already several years ago,⁵ molecular junctions offer fascinating possibilities to adjust thermoelectric properties due to the control over chemical synthesis and interface structure. Ref. 4 and subsequent experimental studies thus explored the influence of different parameters on the thermopower, such as molecule length,^{4,6,7} substituents,⁸ anchoring groups,^{7–9} or electrode metal.¹⁰

On the theory side, the electronic contribution to the thermopower explains important experimental observations.¹¹ We have shown recently that the thermopower of metallic atomic contacts, which serve as reference systems in molecular electronics, can be understood by considering the electronic structure of disordered junction geometries.¹² Using molecular dynamics simulations of many junction stretching processes combined with tight-binding-based electronic structure and transport calculations, we found thermopower-

conductance scatter plots similar to the low-temperature experiment.⁵ Such a statistical analysis, although highly desirable for molecular junctions, is complicated by the time-consuming electronic structure calculations needed to describe these heteroatomic systems. Still, early studies of the thermopower based on density functional theory (DFT) for selected geometries explained crucial trends, such as the dependence of the thermopower on molecule length¹³ or the influence of substituents and anchoring groups.^{13,14} Since the experiments on the thermopower of molecular junctions were all performed at room temperature until now, finite temperature effects may play a role. They can impact the thermopower by fluctuations of the junction geometry and electron-vibration couplings.^{12,15,16} While the quantification constitutes an interesting challenge for future work, we will focus here on the purely electronic effects in static ground-state contact structures.

An interesting aspect, not yet addressed in the experiments is the influence of conjugation on the thermopower Q . For the conductance, such studies were carried out by different groups with biphenyl molecules.^{17–19} The torsion angle φ between the phenyl rings was adjusted stepwise by use of appropriate side groups. While such substituents may have a parasitic shifting effect on energies of current-carrying molecular orbitals, the changes in conformation, which control the degree of π -electron conjugation, turned out to domi-

nate the behavior of the conductance.¹⁷ The systematic series of biphenyl molecules of Refs. 18–21 uses alkyl chains of various lengths and methyl groups to adjust φ and avoids strongly electron-donating and electron-withdrawing substituents. Hence it seems ideal for determining the influence of conjugation on thermopower.

Theoretical work has considered the behavior of Q when φ is changed continuously for the thiolated biphenyl molecule contacted to gold (Au) electrodes.^{13,22} Both studies agree in the fact that Q is positive for all φ . However, while we predicted Q to decrease with increasing φ based on DFT calculations and a π -orbital tight-binding model (TBM),¹³ work of Finch *et al.*²² suggested the opposite for this idealized system. In this study we clarify this contradiction and demonstrate with the help of a two-level model (2LM) that for the off-resonant transport situation the absolute value of Q is expected to decrease when the molecule changes from planar to perpendicular ring orientation. This confirms our previous conclusions. More importantly, this work explores the possibility to measure the dependence of Q on φ for the experimentally relevant family of molecules presented in Refs. 18–21.

Using DFT calculations of the electronic structure combined with the Landauer-Büttiker scattering formalism expressed with Green’s function techniques, we determine the thermopower of biphenyl-derived molecules connected to gold electrodes. The molecules investigated are displayed in Fig. 1. Alkyl chains, one to four CH_2 units long, allow to change φ gradually from 0° to 60° . To achieve $\varphi \approx 90^\circ$, we included in addition M7, and as a reference also M0, the “standard” biphenyl molecule. For each of the molecules in Fig. 1 we will explore the three different anchoring groups sulfur (S), amine (NH_2), and cyano (CN) in various binding geometries.

This work is organized as follows. In Sec. II we introduce the theoretical procedures used in this work. Sec. III presents the main results. We start by discussing models to describe the φ dependence of the thermopower, show the DFT-based results for Q , and provide further insights by discussing their relation to the predictions of the TBM and the 2LM. The paper ends with the conclusions in Sec. IV.

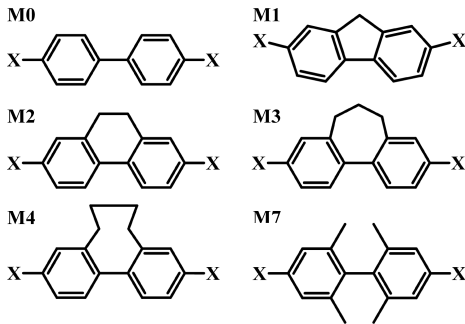


Figure 1: Chemical structure of the studied biphenyl molecules with X standing either for the S, NH_2 , or CN anchoring group.

II. THEORETICAL METHODS

A. Electronic structure and contact geometries

We determine the electronic structure and contact geometries in the framework of DFT. All our calculations are performed with the quantum chemistry package TURBOMOLE 6.3,²³ and we use the gradient-corrected BP86 exchange-correlation functional.^{24,25} For the basis set, we employ def2-SV(P) which is of split-valence quality with polarization functions on all non-hydrogen atoms.²⁶ For Au an effective core potential efficiently deals with the innermost 60 electrons,²⁷ while the basis set provides an all-electron description for the rest of the atoms in this work.

The contact geometries for the S-terminated molecules are those of Ref. 28. For the NH_2 and CN anchors we proceed as described in Refs. 19,28 and use for consistency the electrode geometry from Ref. 28.

B. Charge transport

We determine charge transport properties within the Landauer-Büttiker formalism. The transmission function $\tau(E)$, describing the energy-dependent transmission probability of electrons through the nanostructure, is calculated with non-equilibrium Green’s function techniques. The Green’s functions are constructed by use of the DFT electronic structure as obtained for the ground-state molecular junction geometries. A detailed description of our quantum transport method is given in Ref. 29.

The thermopower at the average temperature T is defined as the ratio of the induced voltage difference ΔV in the steady state and the applied temperature difference ΔT between the ends of a sample, $Q(T) = -(\Delta V/\Delta T)|_{I=0}$. In the Landauer-Büttiker formalism the electronic contribution to the thermopower can be expressed as³⁰

$$Q(T) = -\frac{K_1(T)}{eTK_0(T)} \quad (1)$$

with $K_n(T) = \int dE \tau(E) (E - \mu)^n [-\partial f(E, T)/\partial E]$, the absolute value of the electron charge $e = |e|$, the Fermi function $f(E, T) = \{\exp[(E - \mu)/k_B T] + 1\}^{-1}$, the Boltzmann constant k_B , and the chemical potential $\mu \approx E_F = -5$ eV, which approximately equals the Fermi energy E_F of the Au electrodes. At low temperatures, Eq. (1) simplifies to¹¹

$$Q(T) = -q(T) \left. \frac{\partial_E \tau(E)}{\tau(E)} \right|_{E_F} \quad (2)$$

with the prefactor $q(T) = \pi^2 k_B^2 T / (3e)$ depending linearly on temperature.

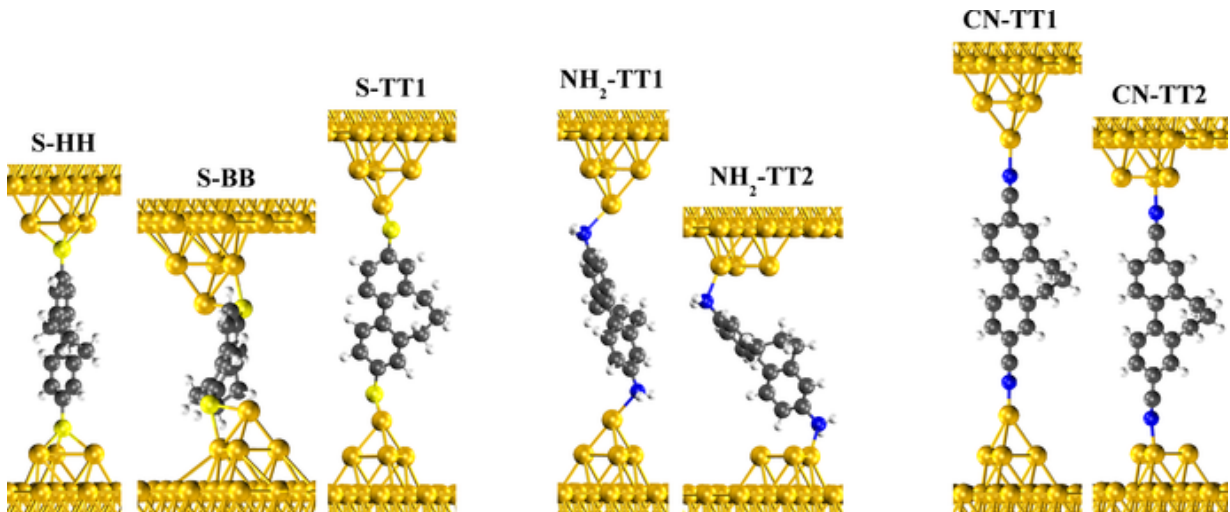


Figure 2: (Color online) Analyzed types of junctions, shown for M3. For S anchors we consider hollow, bridge, and top binding sites to Au with the corresponding contact geometries called S-HH, S-BB, and S-TT1, respectively. For NH_2 and CN we consider binding to single Au atoms in two different top positions with the contacts named NH_2 -TT1, NH_2 -TT2 and CN-TT1, CN-TT2.

	S-HH		S-BB		S-TT1		NH_2 -TT1		NH_2 -TT2		CN-TT1		CN-TT2	
	φ	Q	φ	Q	φ	Q	φ	Q	φ	Q	φ	Q	φ	Q
M0	35.1	0.002	12.9	1.140	17.9	0.907	32.9	0.343	33.2	0.150	33.1	-2.389	35.3	-1.566
M1	0.3	0.064	0.1	1.313	0.4	1.280	0.2	0.436	0.7	0.201	0.7	-2.281	0.1	-1.423
M2	19.8	0.048	19.3	1.208	17.2	1.266	20.4	0.429	19.1	0.191	19.5	-2.252	20.2	-1.404
M3	42.3	0.032	42.1	1.127	42.0	1.200	46.3	0.382	46.3	0.189	45.1	-1.878	46.4	-1.158
M4	60.7	0.034	53.0	1.006	60.8	0.981	61.6	0.400	58.4	0.158	59.2	-1.657	59.9	-0.938
M7	89.6	0.019	84.0	0.298	83.4	0.981	87.4	0.191	87.3	0.091	89.6	-1.173	89.9	-0.632

Table I: Torsion angle φ in units of degrees and the thermopower Q at $T = 10$ K in units of $\mu\text{V}/\text{K}$ for all junction geometries.

In the following the thermopower is calculated, if not otherwise indicated, for a low temperature of $T = 10$ K, where our theory is expected to apply best. For the DFT-based results presented below we determine Q by means of Eq. (1), i.e. by taking into account the thermal broadening of the electrodes. For the molecular junctions studied here, the differences to the values obtained via Eq. (2) often turn out to be small even at room temperature ($T = 300$ K). Hence thermopower values for higher T can be estimated using the values at 10 K through $Q(T) \approx (T/10 \text{ K}) \times Q(10 \text{ K})$. Since we are not primarily interested in the temperature dependence of Q in this work, we suppress from here on the temperature argument.

III. RESULTS AND DISCUSSION

A. Models for the angle-dependent thermopower

In Ref. 13 we argued that the thermopower should depend on the torsion angle as

$$Q_\varphi \approx a + b \cos^2 \varphi. \quad (3)$$

Our argument was based on the observation that for a π -orbital TBM in the off-resonant transport situation, the transmission of the biphenyl molecule can be expanded in powers of $\cos^2 \varphi$ as^{13,31,32}

$$\tau_\varphi(E) = \alpha_2(E) \cos^2 \varphi + \alpha_4(E) \cos^4 \varphi + O(\cos^6 \varphi). \quad (4)$$

Conductance measurements^{17–19} and corresponding DFT calculations,³¹ which both determine the transmission at the Fermi energy, show that α_2 is the dominant term. The leading term in the φ dependence of Q is obtained from Eq. (2) by taking into account the energy dependence of the expansion coefficients $\alpha_j(E)$ and considering the terms up to $j = 4$. Then, we obtain Eq. (3) with

$$a = -q \left. \frac{\partial_E \alpha_2(E)}{\alpha_2(E)} \right|_{E=E_F}, \quad (5)$$

$$b = -q \left. \frac{\alpha_2(E) \partial_E \alpha_4(E) - \alpha_4(E) \partial_E \alpha_2(E)}{\alpha_2(E)^2} \right|_{E=E_F}. \quad (6)$$

While this model uses minimal information about the biphenyl molecular junction, a disadvantage is that the magnitude and energy dependence of the coefficients α_2 and α_4 are a priori unknown.

An alternative strategy is to use the 2LM of Ref. 18. This minimal model explains the $\cos^2 \varphi$ law of the conductance by considering the pair of hybridizing frontier orbital resonances of the phenyl rings which are closest to E_F . Within this model, the transmission is given by¹⁸

$$\tau_\varphi(E) = \left| \frac{\tilde{\Gamma} \tilde{t} \cos \varphi}{(E - \tilde{\varepsilon}_s(\varphi) - i\tilde{\Gamma}/2)(E - \tilde{\varepsilon}_a(\varphi) - i\tilde{\Gamma}/2)} \right|^2 \quad (7)$$

with $\tilde{\varepsilon}_{s,a}(\varphi) = \tilde{\varepsilon}_0 \pm \tilde{t} \cos \varphi$. Here, $\tilde{\varepsilon}_0$ is the relevant frontier molecular orbital energy of the individual phenyl ring. For the biphenyl molecule, it can be determined as the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) energy for vanishing inter-ring coupling $\tilde{t} \cos \varphi$ at $\varphi = 90^\circ$. The angle-dependent inter-ring coupling leads to a splitting of the pair of degenerate levels $\tilde{\varepsilon}_0$ at energies $\tilde{\varepsilon}_{s,a}(\varphi) = \tilde{\varepsilon}_0 \pm \tilde{t} \cos \varphi$ with symmetric and antisymmetric wavefunctions, respectively. In addition, we have made the wide-band approximation with a symmetric and energy-independent coupling $\tilde{\Gamma}$ to the left and right phenyl rings. The 2LM is hence characterized by the parameters $\tilde{\varepsilon}_0, \tilde{t}, \tilde{\Gamma}$.

We set $\tilde{\varepsilon} = \tilde{\varepsilon}_0 - E_F$, $\tilde{x} = \tilde{t} \cos \varphi / \sqrt{\tilde{\varepsilon}^2 + \tilde{\Gamma}^2/4}$, and assume $|\tilde{x}| \ll 1$. Performing a Taylor expansion in \tilde{x} , we obtain Eq. (3) with

$$a = -q \frac{4\tilde{\varepsilon}}{\tilde{\varepsilon}^2 + \tilde{\Gamma}^2/4}, \quad (8)$$

$$b = -q \frac{4\tilde{t}^2 \tilde{\varepsilon} (\tilde{\varepsilon}^2 - 3\tilde{\Gamma}^2/4)}{(\tilde{\varepsilon}^2 + \tilde{\Gamma}^2/4)^3}. \quad (9)$$

These expressions predict that the sign of a, b is determined by $\tilde{\varepsilon}$. Thus, when $\tilde{\varepsilon}$ changes sign, a, b change sign at the same time. In the typical off-resonant transport situation $|\tilde{\varepsilon}| \gg |\tilde{t}|, \tilde{\Gamma}$, the sign of $a \approx -q4/\tilde{\varepsilon}$ and $b \approx -q4\tilde{t}^2/\tilde{\varepsilon}^3$ is identical. However, b may be of a different sign than a in a more on-resonant case when the broadening $\tilde{\Gamma}$ is of a similar size as $\tilde{\varepsilon}$, i.e., when $\tilde{\varepsilon}^2 - 3\tilde{\Gamma}^2/4$ changes sign.

B. Thermopower based on density functional theory

For each of the biphenyl molecules in Fig. 1, we study the three different anchoring groups $X = S, \text{NH}_2, \text{CN}$ and select a total of seven contact geometries, as displayed in Fig. 2. For S anchors we choose three representative binding sites,^{28,33} where S binds covalently either to three Au atoms in the hollow position (S-HH), to two of them in the bridge position (S-BB), or to a single one in the top position (S-TT1). NH_2 - and CN-terminated molecules bind selectively to a single Au electrode atom at each side via the nitrogen lone pair.^{19,34} Thus, we consider

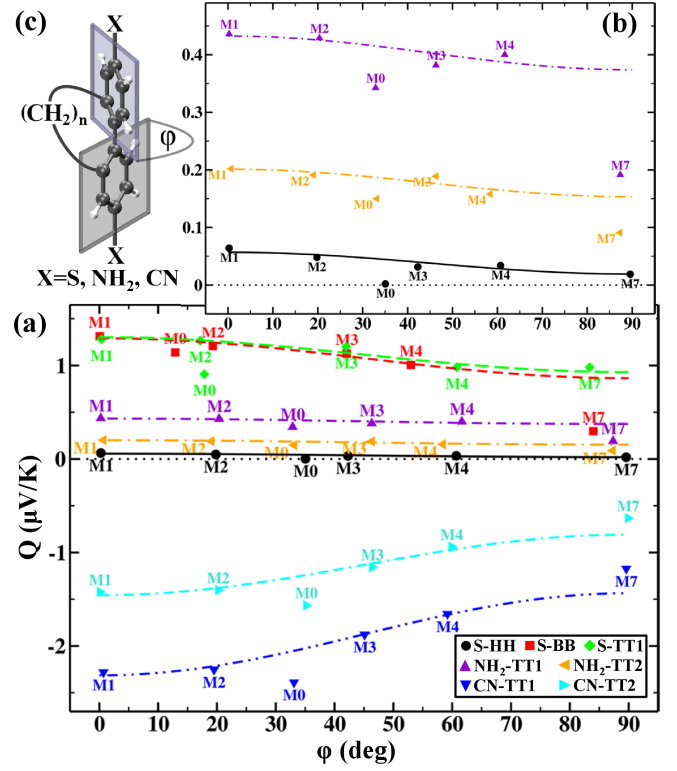


Figure 3: (Color online) (a) Evolution of Q with increasing φ for all contact geometries. The symbols represent the thermopower values calculated with DFT at $T = 10$ K, and the lines are obtained by fitting Eq. (3) to M1-M4 for each type of junction. (b) Zoom in on the Q values for S-HH, NH_2 -TT1, and NH_2 -TT2. (c) Schematic of the studied biphenyl derivatives and definition of the torsion angle φ .

two different top sites for NH_2 (NH_2 -TT1, NH_2 -TT2) and CN (CN -TT1, CN -TT2), respectively.

In Table I we summarize the torsion angle φ , which is defined as the dihedral angle between the two phenyl rings (see Fig. 3), and the thermopower for all 42 molecular junctions studied. The data is presented graphically in Fig. 3 by plotting Q as a function of φ for each of the seven types of junctions in Fig. 2. We notice that the sign of the thermopower is determined by the anchoring group. For the electron-donating S and NH_2 linkers³⁵ the energy of the π -electron system of the molecules is increased compared to the hydrogen-terminated case ($X = \text{H}$ in Fig. 1). The HOMO energy is therefore close to E_F , as visible also from the transmission curves in Fig. 4. The hole conduction through the HOMO yields $Q > 0$, in agreement with previous experimental^{4,6} and theoretical results.^{13,14} In contrast to this, for the electron-withdrawing CN anchoring group³⁵ we have electron transport through the LUMO^{8,14,19,36} (see also Fig. 4), and consequently $Q < 0$.

Considering the absolute values of the thermopower, Fig. 3 shows that Q can differ markedly for the types of contact geometries. Given the off-resonant transport situation suggested by the transmission curves in Fig. 4

and using Eqs. (8) and (9), we can understand the results by changes in the level alignment $\tilde{\varepsilon}$. As we will discuss in more detail below in Sec. III C, level broadenings $\tilde{\Gamma}$ and couplings \tilde{t} play no important role in that respect. The level alignment is determined by the charge transfer between the molecule and the electrodes, which is sensitive to the binding site of the anchoring group at the molecule-metal interface. For the thiolated molecules we find that the thermopower for S-BB and S-TT1 is comparable, but the values are significantly larger than those for S-HH. This behavior is related to our recent findings for the conductance of the thiolated molecules, where top and bridge geometries yield similar but much larger conductances than those with hollow sites.²⁸ Both observations are due to a HOMO level which is more distant from E_F for S-HH as compared to S-BB and S-TT1. We explain this by the leakage of electrons from the molecule, including the S atoms, to the Au electrodes, when going from the S-TT1 over the S-BB to the S-HH geometry.²⁸ For the amines NH₂-TT1 gives a larger thermopower than NH₂-TT2. We have checked that this is a result of the larger negative charge on the molecule when bonded in NH₂-TT1 position as compared to NH₂-TT2, which moves the HOMO closer to E_F . With respect to the thiols we see that both NH₂-linked geometries give rise to a thermopower well below those of S-BB and S-TT1 but still larger than for S-HH. The CN-linked molecules show the largest $|Q|$. The more positive charge on the molecules in CN-TT1 as compared to CN-TT2 leads to their smaller, i.e., more negative Q .

Regarding M0 with X = S, NH₂ we can compare to experimental and theoretical results for Q in the literature. For biphenyl-diamine a thermopower of $Q_{M0}^{NH_2-EXP} = 4.9 \pm 1.9 \mu V/K$ was found at $T = 300 K$,⁶ which compares reasonably well to our calculated values of $Q_{M0}^{NH_2-TT1} = 10.52 \mu V/K$ and $Q_{M0}^{NH_2-TT2} = 4.6 \mu V/K$ for the same T . Furthermore, recent calculations within a DFT approach with an approximate self-interaction correction for comparable geometries showed similar results to ours.³⁷ For biphenyl-dithiol the comparison is complicated by the fact that our calculated values vary by two orders of magnitude for the different geometries, i.e., $Q_{M0}^{S-HH} = 0.11 \mu V/K$, $Q_{M0}^{S-BB} = 39.14 \mu V/K$, $Q_{M0}^{S-TT} = 28.08 \mu V/K$ at $T = 300 K$. They scatter indeed around the experimental result of $Q_{M0}^{S-EXP} = 12.9 \pm 2.2 \mu V/K$.⁴ To our knowledge, the thermopower of cyano-terminated biphenyls has not yet been reported. A trend by the DFT calculations to overestimate the thermopower can nevertheless be recognized.³⁷ It is expected from the typical overestimation of experimental conductance values,²⁸ attributed mostly to the interpretation of Kohn-Sham eigenvalues as approximate quasi-particle energies.^{38,39} According to Eqs. (8) and (9) an underestimation of $|\tilde{\varepsilon}|$ leads to an overestimation of $|Q|$. However, finite temperature effects due to vibrations, not accounted for in our calculations, may also play a role in the room-temperature experiments.

The transport through the well-conjugated molecules

	$a (\mu V/K)$	$b (\mu V/K)$	$r (\%)$
S-HH	0.02	0.04	31
S-BB	0.86	0.43	13
S-TT1	0.93	0.37	13
NH ₂ -TT1	0.37	0.06	4
NH ₂ -TT2	0.15	0.05	12
CN-TT1	-1.44	-0.89	16
CN-TT2	-0.81	-0.65	20

Table II: Parameters a and b of Eq. (3) used in Fig. 3 to fit the DFT results of M1-M4 for each type of junction, and the relative change r of Q between M1 and M4.

M0-M4 is dominated by the π electrons, and we have shown in Refs. 18,19,28 that for these molecules the conductance arises from one transmission eigenchannel of π character.^{19,28} Hence we would expect their thermopower to follow Eq. (3). Despite the variations of Q with anchoring groups and binding positions, we find a weak $\cos^2\varphi$ -like decrease of the absolute values for M1-M4 for all types of geometries. M0, however, deviates from this trend. Although the electron-donating effect of the alkyl chains is expected to be small, it increases Q for M1-M4 as compared to M0. To clarify this we calculated by means of electrostatic potential fitting and a Löwdin population analysis the charge transferred from the alkyl side chains to the two phenyl rings for the hydrogen-terminated (X = H in Fig. 1), isolated gas-phase molecules. Both methods yield an overall negative charge on the phenyl rings which is practically independent of the alkyl chain length. Therefore the substituent-related energy shift of frontier orbital levels is similar for M1-M4, and the $a + b \cos^2\varphi$ dependence is observed.

Focusing on the thermopower of M1-M4, we extract a and b by fitting their Q with Eq. (3). The precise values are given in Table II, and the corresponding fits are shown as continuous lines in Fig. 3. Additionally, we list in Table II the ratio $r = |Q_{M1} - Q_{M4}| / (Q_{M1} + Q_{M4})$, quantifying the maximal decrease of Q in that subset of molecules. We find it to vary between 4% and 31%. In detail, we observe the largest relative change for S-HH followed by CN-TT2. CN-TT1, S-BB, S-TT1, and NH₂-TT2 all show a similar r , while it is smallest for NH₂-TT1.

For M7, Eq. (3) is not expected to hold, because the transport at $\varphi \simeq 90^\circ$ is not π -like but proceeds through transmission eigenchannels of π - σ character.^{13,28} Furthermore, M7 shows the largest substituent-related shifting effect on the biphenyl backbone in our family of molecules due to the electron-donating nature of the four attached methyl side-groups.^{13,35,40} Its thermopower hence arises from a detailed interplay between the substituent-related shifting and the large torsion angle, as explained in Ref. 13. We find that the absolute values of Q for M7 are generally lower than predicted by the fits with Eq. (3). Only for S-TT1 and NH₂-TT2 the thermopower seems to follow the $a + b \cos^2\varphi$ dependence

but this is likely coincidental.

C. Transport analysis using the π -orbital tight-binding model and the two-level model

In order to better understand the differences in the thermopower for the various anchoring groups and binding positions, we need to examine the parameters $\tilde{\varepsilon}$, \tilde{t} , $\tilde{\Gamma}$ of the 2LM which determine the thermopower according to Eqs. (8) and (9). We note that the dominant, angle-independent term a is a function of $\tilde{\varepsilon}$, $\tilde{\Gamma}$ only. Thus, to discuss main anchor-group- and binding-site-related variations of Q for the seven different junction types of Fig. 2, it is sufficient to concentrate on these two parameters. The φ dependence of Q , however, results from the interference of the hybridizing pair of phenyl-ring frontier orbital levels, and b hence depends also on \tilde{t} .

We obtain the parameters of the 2LM from the TBM introduced in Ref. 32. The TBM is sketched in Fig. 4(a). Similar to the 2LM, the Hückel-like TBM is characterized by three parameters which are the on-site energy ε_0 of each carbon atom, the nearest-neighbor hopping t between atoms on each of the phenyl rings, and the electrode-related broadening Γ . The inter-ring hopping is given as $t' = t \cos \varphi$. Using the wide-band approximation, we assume all components of the lead self-energy matrices to vanish except for $(\Sigma_L^r)_{\alpha\alpha} = (\Sigma_R^r)_{\omega\omega} = -i\Gamma/2$, with α and ω indicating the terminal carbon atoms of the biphenyl molecule as shown in Fig. 4(a).

The parameters ε_0, t, Γ of the TBM are extracted by fitting $\tau(E)$ curves calculated with DFT. We focus on the molecules M1-M4 and set φ to the torsion angle realized in the specific junction geometry (see Table I). Concentrating particularly on the HOMO-LUMO gap and frontier orbital peaks, we find that the fitted TBM generally reproduces well the transmission in that range and that the parameters extracted for M1-M4 are very similar in each of the seven types of junctions. Finally, the parameters of the 2LM are derived from those of the TBM. $\tilde{\varepsilon}$ and \tilde{t} are obtained by evaluating appropriate eigenvalues of the angle-dependent Hückel-like Hamiltonian of the TBM. For $\tilde{\Gamma}$ we identify imaginary parts of complex eigenvalues of the non-Hermitian matrices $(H + \Sigma_L^r + \Sigma_R^r)_{jk}$ for the TBM and the 2LM, respectively.²⁸ Here, H_{jk} and $(\Sigma_L^r)_{jk}, (\Sigma_R^r)_{jk}$ represent the matrix elements of the Hamiltonian and of the electrode self-energies in the corresponding model. All the parameters determined in this way are listed in Table III. For M2, transmission curves calculated with the DFT, the TBM, and the 2LM are shown in Fig. 4(b) for each of the three anchoring groups.

Using the parameters of Table III we compare in Fig. 4(c) Q as a function of φ for the TBM and 2LM fits with the DFT results. We find that the TBM agrees well with the DFT-based values for the illustrated junction geometries S-TT1, NH₂-TT1, and CN-TT2. The 2LM, instead, overestimates $|Q|$ somewhat. Considering

	ε_0	t	Γ	$\tilde{\varepsilon}$	\tilde{t}	$\tilde{\Gamma}$
S-HH	-4.40	-2.30	0.70	-1.70	-0.68	0.22
S-BB	-4.02	-1.95	1.10	-0.97	-0.58	0.35
S-TT1	-4.00	-1.90	0.96	-0.90	-0.56	0.31
NH ₂ -TT1	-4.30	-2.29	0.60	-1.59	-0.68	0.19
NH ₂ -TT2	-4.40	-2.32	0.66	-1.72	-0.69	0.21
CN-TT1	-6.10	-2.00	0.14	0.90	-0.59	0.04
CN-TT2	-6.05	-1.99	0.15	0.94	-0.59	0.05

Table III: Parameters of the TBM ε_0, t, Γ obtained by fitting the DFT-based transmission curves for M1-M4 for each type of junction. The parameters $\tilde{\varepsilon}, \tilde{t}, \tilde{\Gamma}$ of the 2LM are derived from those of the TBM as described in the text. All values are given in units of eV.

Eq. (2) and the transmission curves in Fig. 4(b), we attribute this to an underestimation of $\tau(E_F)$ and an overestimation of $|\partial_E \tau(E_F)|$. All results exhibit a consistent weak dependence of Q on φ .

The data in Table III shows that transport through the biphenyl molecules is off-resonant with the relation $\tilde{\Gamma} \ll |\tilde{\varepsilon}|$ being well fulfilled. As argued in Sec. III A, a, b should thus take the same sign and change it together with Q when the transport for S- and NH₂-linked molecules changes from HOMO- to LUMO-dominated for CN anchors. This is consistent with our findings in Figs. 3 and 4(c), and explains the decrease of $|Q|$ with increasing φ .⁴¹

Coming back to our discussion of the differences of the thermopower for the various anchoring groups and binding positions in Fig. 3, we observe that $\tilde{\varepsilon}$ is around 0.6 to 0.8 eV closer to E_F for S-BB and S-TT1 as compared to S-HH, NH₂-TT1, and NH₂-TT2, which explains their larger Q . For the CN-terminated molecules $|\tilde{\varepsilon}|$ is comparable to those for S-BB and S-TT1. Slightly larger values of $|Q|$ for CN result from the very small broadenings $\tilde{\Gamma}$. Furthermore, for both NH₂ and CN, \tilde{t} and $\tilde{\Gamma}$ are essentially independent of the binding position, and the difference in Q between TT1 and TT2 hence stems from the changes in the alignment of the HOMO and LUMO levels.

IV. CONCLUSIONS

We have analyzed theoretically the thermopower of single-molecule junctions consisting of biphenyl derivatives contacted to gold electrodes. Our DFT-based study with the three anchors S, NH₂, and CN shows a positive thermopower for S or NH₂ and a negative one for CN. For the junction geometries considered, different binding sites did not affect the sign of Q but led to variations of absolute value. For thiolated molecules in bridge and top binding sites Q can be up to two orders of magnitude larger than for molecules bonded in hollow position, while the variations for the two considered top binding sites

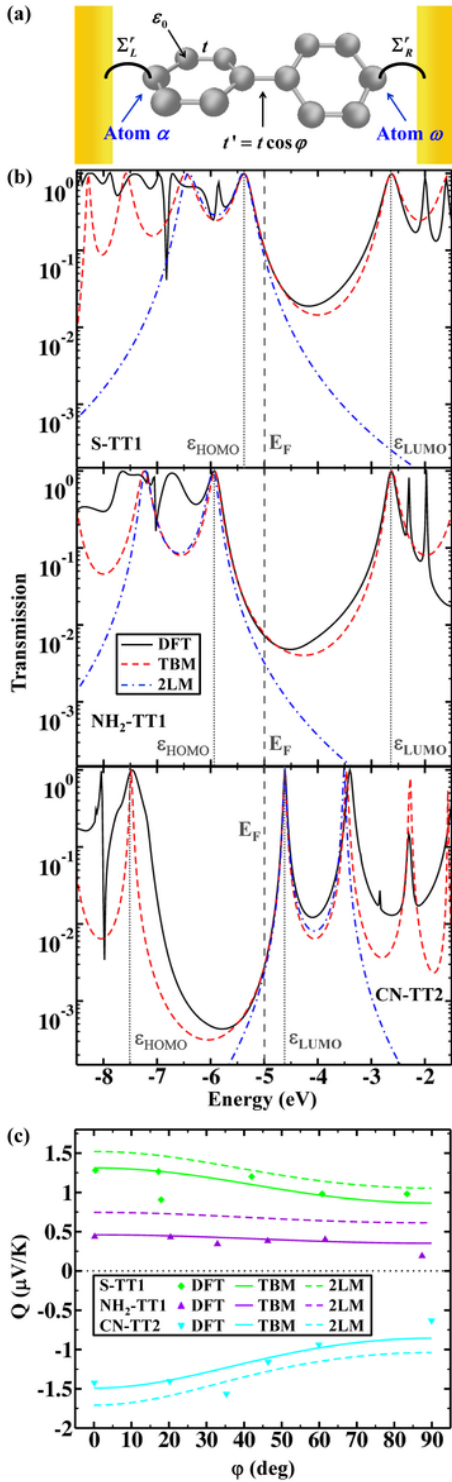


Figure 4: (Color online) (a) Schematic of the TBM used to fit DFT-based transmission curves. (b) Transmission of M2 as a function of energy calculated with DFT, and the fits using the TBM and the 2LM. (c) Q as a function of φ , comparing values obtained with the TBM and the 2LM to the DFT-based results. In panels (b) and (c) S-TT1, NH₂-TT1, and CN-TT2 junction geometries were selected.

were around a factor of two for NH₂ and CN anchors. We have explained these observations by the changes in the level alignment of current-carrying frontier molecular orbitals. They are caused by the binding-site-dependent charge transfer at the metal-molecule interface.

The main purpose of this work was the study of the dependence of the thermopower on conjugation for an experimentally relevant system. In our set of six biphenyl derivatives, the conjugation was controlled by the torsion angle φ between the phenyl ring planes, and it was varied stepwise between 0 and 90° by means of alkyl side chains attached to the molecules. Despite the sensitivity of the thermopower to the precise geometry at the molecule-metal interface, we observed for all investigated types of junction configurations a decrease in $|Q|$ with increasing φ , following a characteristic $a + b \cos^2 \varphi$ law. We explained this behavior in terms of a two-level model, which considers the pair of hybridizing frontier orbitals on the phenyl rings. Predictions by this model of a simultaneous change in sign of Q , a , b for a change from HOMO- to LUMO-dominated transport in the off-resonant situation are consistent with our DFT results. Overall, the influence of conjugation on the thermopower is much less pronounced than on the conductance.

We propose to measure the $a + b \cos^2 \varphi$ dependence of the thermopower for the set of biphenyl molecules studied here. Using alkyl chains of different lengths, parasitic substituent-related shifts in Q , superimposed on the weak $a + b \cos^2 \varphi$ dependence, are largely avoided. Depending on binding site and employed anchoring group, relative variations of Q of around 15% are expected between M1 and M4. Since frontier molecular orbital energies are likely positioned closer to E_F in our calculations than in the experiment, the relative changes of Q with φ are expected to be somewhat smaller than in our theoretical predictions. Nevertheless, we suggest that the variations of the thermopower with torsion angle are experimentally detectable.

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